

# Electron Transfer Reactions in Organic Chemistry. XX.\*† Fate of Tris(4-bromophenyl)ammoniumyl Hexachloroantimonate During Catalysis of the Diels–Alder Dimerization of 1,3-Cyclohexadiene

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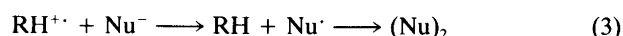
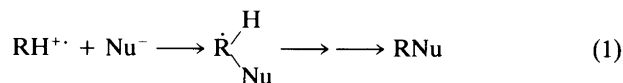
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The Diels–Alder (DA) dimerization of 1,3-cyclohexadiene (CHD) by the radical cation salt, tris(4-bromophenyl)ammoniumyl hexachloroantimonate (TBPA<sup>+</sup>·SbCl<sub>6</sub><sup>-</sup>), has been studied by kinetic methods and product identification. The main goal was to elucidate the pathways by which TBPA<sup>+</sup>· is consumed. These can be summarized as follows. In the absence of any added base, DA dimers are formed in high yield and the radical cation is consumed in an essentially quantitative oxidative addition reaction between CHD<sup>+</sup>· and a chloride ion source, most likely hexachloroantimonate ion. In the presence of a hindered pyridine base, DA dimerization is almost blocked and CHD<sup>+</sup>· is deprotonated by the base ultimately to give benzene (up to 40% yield) and oligomers of CHD. Thus in both cases the role of TBPA<sup>+</sup>· is to abstract an electron from CHD, the radical cation of which is presumably the product-forming species.

The mechanism is complex, but it could be shown that DA dimerization is second-order in [CHD] under the hypothetical conditions that [TBPA<sup>+</sup>·]/[TBPA] is constant. It is assumed (and supported by Marcus-type calculations) that the reduction of the dimer radical cation, (CHD)<sub>2</sub><sup>+</sup>·, occurs via reaction with TBPA, thus making the mechanism of rather conventional catalytic type. TBPA is formed to an extent of > 50% in the very early part of the run. The measured rate constant, *k*(CHD)<sub>obs</sub>, is then proportional to [TBPA<sup>+</sup>·]<sub>0</sub>/[TBPA]<sub>∞</sub>. The disappearance of the radical cation via the oxidative addition process was second order in [TBPA<sup>+</sup>·], indicative of the so-called complexation mechanism for radical cation/nucleophile reactions.

A radical cation can react with a nucleophile/base/reductant either as an electrophile/acid or with electron transfer (ET),<sup>2–5</sup> as shown schematically in eqns. (1)–(3). A specific, very common electrophilic reaction mode of radical cations is coupling with a neutral unsaturated hydrocarbon, eventually leading to C–C bond formation between the two components [analogously to eqn. (1), with Nu<sup>-</sup> = RH or RH’]. This mechanism is often denoted the RSC (Radical cation–Substrate Coupling) mechanism. Many examples of such reactions are known, both involving aromatic and olefinic compounds, with most applications from organic electrochemistry. Finally, a radical cation can undergo the RRD (Radical cation–Radical cation Dimerization) mechanism, as shown in eqn. (4).

The archetypal ET reagent, tris(4-bromophenyl)ammoniumyl (TBPA<sup>+</sup>·), commonly used as an ET oxidant/catalyst,<sup>6</sup> has been shown to possess the same blend of electro-



philic/radical/ET reactivity.<sup>7–10</sup> It undergoes acetoxylation, chlorination or cyanation in the 2-position upon reaction with acetate,<sup>5</sup> chloride or cyanide ion, respectively.<sup>8</sup> Thus TBPA<sup>+</sup>· behaves as an electrophile in these reactions, well known from many applications of anodic oxidative sub-

<sup>5</sup> Based upon electrochemical evidence, it was recently claimed<sup>11</sup> that TBPA<sup>+</sup>· reacts with acetate ion in a clean one-electron transfer process, whereas the reaction with hydrogendiacetate ion leads to nuclear acetoxylation. Product studies however show that both species give acetoxylation products with TBPA<sup>+</sup>· and < 10<sup>-3</sup>% yield of one-electron derived products<sup>10</sup> (ethane, methane). Similar product studies have been carried out for 9-phenylanthracene radical cation by Parker *et al.*<sup>12</sup> Consequently, the analysis of the electrochemical oxidation of TBPA in the presence of acetate ion in terms of a catalytic mechanism, leading to one-electron oxidation of acetate ion,<sup>13</sup> is incompatible with our product studies.

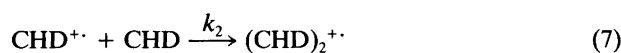
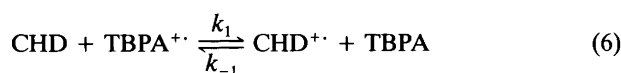
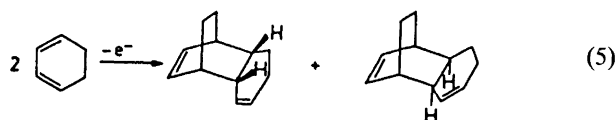
\* Part XIX, see Ref. 1.

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stitution of a wide variety of substrates.<sup>2,3</sup> On the other hand, it cleanly oxidizes bromide or iodide ion according to an ET mechanism.<sup>8</sup> This is normal behaviour for a radical cation, insofar as normal behaviour can be defined for this class of intermediates. TBPA<sup>•+</sup> also undergoes the RRD/RSC mechanism by *ipso* coupling via the 4-position,<sup>7</sup> giving a dication with brominating properties. We initially suggested<sup>7</sup> an RRD mechanism for this step but realize that a more detailed analysis might make the RSC alternative more likely, as suggested by Pletcher and Zappi.<sup>14</sup> As usual, there is an electrostatic argument against the RRD mechanism, even though it does not exclude it, as seen from a recent theoretical study of anion radical dimerization.<sup>15</sup>

In view of the normal reactivity of TBPA<sup>•+</sup> in comparison with other radical cations, its ability to catalyse Diels–Alder (DA) reactions according to what has been assumed to be an ET-catalysed radical cation chain mechanism,<sup>6,16</sup> represents a deviation. The most intensively studied reaction of this type is the DA dimerization of 1,3-cyclohexadiene (CHD), shown in eqn. (5) and postulated to follow the radical chain mechanism of eqns. (6)–(8).<sup>16</sup> Two unexpected features stand out, namely (i) TBPA<sup>•+</sup> does not couple with CHD and (ii) CHD<sup>•+</sup> does not seem to



undergo proton abstraction [eqn. (2)], even in the presence of non-nucleophilic bases, such as 2,6-di-*tert*-butylpyridine, otherwise a very fast reaction mode of radical cations.<sup>5</sup> This would eventually give benzene after a second electron transfer and proton abstraction. Another possibility would be the formation of dehydro-oligomerized products. We became interested in these anomalies and decided to examine the mechanism of the TBPA<sup>•+</sup>/CHD reaction in more detail. We now show that this system is far more complex than is normally assumed. The radical cation is consumed in oxidation processes with CHD, namely formation of benzene/oligomers in the presence of a hindered base and formation of oxidative chloro adducts in the absence of external base. The mechanism of DA dimer formation is probably not of the radical chain type but instead follows a more conventional catalytic pathway.

## Results and discussion

**Thermal dimerization of CHD.** Since the published<sup>6a,16</sup> rate comparison between the TBPA<sup>•+</sup>-catalysed and thermal dimerization of CHD is based on an essentially qualitative study of the thermal process [‘30 % yield of Diels–Alder (DA) dimers after 20 h at 200 °C’], we first measured the rate of CHD dimerization in the liquid phase at 120 and 200 °C. As expected, the reaction reached an equilibrium after a relatively short time. This occurred at a level of 60 % DA dimers after only ca. 3 h at 200 °C; the concentration of DA dimers then slowly decreased owing to formation of higher oligomers (Fig. 1). The dimerization rate constants for reaching equilibrium<sup>17</sup> in neat CHD at 120 and 200 °C were  $1.4 \times 10^{-7}$  and  $1.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ , respectively, from which the activation energy could be calculated to be 22 kcal mol<sup>-1</sup>. At 120 °C, the rate constant for CHD dimerization in dichloromethane was lower by a factor of ca. 3, or  $5 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$ .

This can be compared to the gas-phase data for CHD dimerization published by De Mare *et al.*<sup>18</sup> from which the rate constant for formation of the DA dimers at 200 °C was calculated to be  $1.0 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ , agreeing with the above liquid-phase value to within a factor of 1.5. The gas-phase activation energy was 24.7 kcal mol<sup>-1</sup>, which means that the rate constant at 120 °C,  $5 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$ , is ca. three times lower than the liquid-phase value.

These kinetic parameters will be compared below with those of the radical cation catalysed process.

**Product analysis. What happens to TBPA<sup>•+</sup>?** At the outset, we stress that the purpose of our studies is to elucidate the reactivity of TBPA<sup>•+</sup> under different conditions. The radical chain mechanism proposed [eqns. (6)–(8)] for the DA dimerization of CHD in principle does not use up any of the radical cation, nor does the alternative conventionally catalytic pathway obtained by replacing eqn. (8) by eqn. (9), reoxidation of TBPA by the dimer radical cation (because of the ease of oxidation of TBPA as compared with that of CHD this possibility must be considered seriously; see calculations below indicating that  $k_3$  is in the diffusion-controlled range).

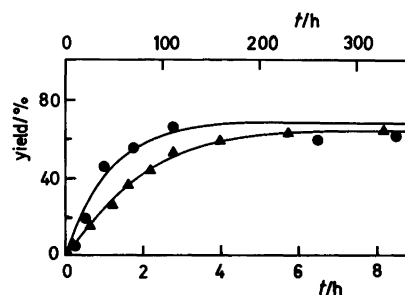


Fig. 1. Time ( $t$ ) dependence of the yield of DA dimers from neat CHD at 200 (●, lower time scale) and 120 (▲, upper time scale) °C.

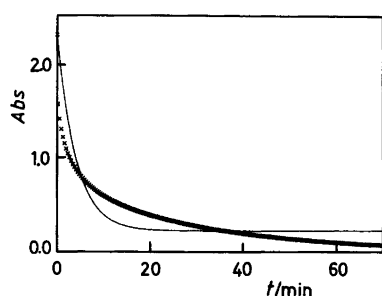


Fig. 2. Decay (x) of a 0.4 mM solution of  $\text{TBPA}^{+\cdot} \text{SbCl}_6^-$  in dichloromethane at 20°C upon addition of CHD in an initial concentration of 8.0 mM, as monitored at  $\lambda = 728 \text{ nm}$ . The solid curve represents the best fit of an exponential curve to the data points.



Yet, the most conspicuous feature of the reaction is the rapid disappearance of  $\text{TBPA}^{+\cdot}$ , especially in the initial phase of the reaction, as easily monitored by the decrease in absorbance at 728 nm (Fig. 2) and shown by the formation of > 95% yield of TBPA (UV, GLC). This reaction does not follow a first-order rate dependence (Fig. 2). Addition of a hindered base, 2,6-di(*tert*-butyl)pyridine, strongly enhanced the rate of decay of  $\text{TBPA}^{+\cdot}$ , and the reaction became first order in the radical cation. We initially assumed that the reaction modes ultimately responsible for the decay of the radical cation might be loss of an  $\alpha$  proton [eqn. (2)] from  $\text{CHD}^{+\cdot}$ , followed by a second ET step to give the cyclohexadienyl cation, a species with a high driving force to lose a proton to give benzene, and/or possibly an RSC coupling with CHD to give eventually a dehydromer of CHD. The latter type of product was however not detected.

Unless specifically sought, benzene would not be easily detectable at the 5–10 mol % level of catalyst that is normally used, since the maximum yield of benzene would be 2.5–5% which would have to be analysed in the pres-

ence of a large excess of CHD containing an inevitable background level of ca. 1.5% of benzene. Such reaction paths are also indicated by the fact that the catalysis of the Diels–Alder reaction needs a relatively large amount of the radical cation catalyst<sup>6,19</sup> (up to 50 mol %) in the presence of a hindered base. Other, related possibilities for loss of oxidant would be carbocation or radical cation propagated oligomerization of CHD.<sup>20</sup> In either case there is a net consumption of two moles of  $\text{TBPA}^{+\cdot}$  per mol of CHD oxidized.

An initial product study showed (Fig. 3) that the yield of the Diels–Alder (DA) dimer decreases strongly with addition of increasing amounts of a hindered base, 2,6-di(*tert*-butyl)pyridine, but the yield seems to level off at around 10% at high [base]/[ $\text{TBPA}^{+\cdot}$ ] ratios. Bauld *et al.*<sup>21</sup> reported almost complete suppression of the DA reaction at a [base]/[ $\text{TBPA}^{+\cdot}$ ] ratio of only 1, whereas at a ratio of 4 Gassman and Singleton<sup>19</sup> found a 27% yield of the DA dimer and 62% unchanged CHD. The analytical procedure was then extended to allow for the analysis of benzene as well. The CHD contained a background level of 1.5 mol % of benzene, which was subtracted from the analyses of the reaction mixtures. Table 1 shows these results. Two sets of conditions were used, namely those employed in prep-

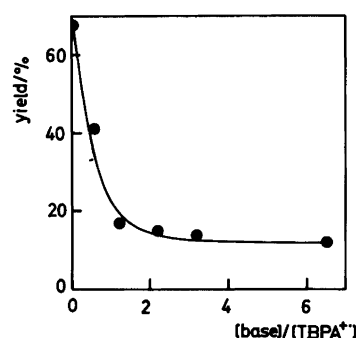


Fig. 3. Yield of DA dimers as a function of [base]/[ $\text{TBPA}^{+\cdot}$ ] in dichloromethane at 0°C.  $[\text{CHD}]_0 = 190 \text{ mM}$ ;  $[\text{TBPA}^{+\cdot}]_0 = 9.2 \text{ mM}$ ; 2,6-di(*tert*-butyl)pyridine = base. Conditions were heterogeneous.

Table 1. Products formed from the reaction between  $\text{TBPA}^{+\cdot} \text{SbCl}_6^-$  and CHD in dichloromethane at 0°C in the presence of a hindered base. The base is 2,6-di(*tert*-butyl)pyridine, unless otherwise stated.

[ $\text{TBPA}^{+\cdot}$ ]/mM	[CHD]/mM	[Base]/[ $\text{TBPA}^{+\cdot}$ ]	Unchanged CHD (%)	Benzene yield (%) <sup>a</sup>	DA-dimer yield (%)	<i>endo</i> / <i>exo</i>	Remark <sup>b</sup>
9.2	190	0	2	ca. 0	70		Het
9.2	190	1.2	73	26	20		Het
9.2	190	6.5	77	26	15		Het
9.2	190	6.5 <sup>c</sup>	93	43	5		Het
46	190	1.2	11	22	67		Het
0.8	16	0	11	ca. 0	88	6.4	Hom
0.8	16	0.5	27	28	67	6.0	Hom
0.8	16	1.1	81	32	17	5.0	Hom
0.8	16	2.0	79	31	17	5.1	Hom

<sup>a</sup>Based on the amount of radical cation and calculated for a two-electron reaction. <sup>b</sup>Het = heterogeneous, Hom = homogeneous system. <sup>c</sup>The base was 2,6-lutidine.

arative runs (ca. 0.2 M in [CHD], 5 mol % of the radical cation catalyst) in which the radical cation salt was not completely dissolved, and homogeneous solution conditions which however suffer from the disadvantage that concentrations become uncomfortably low for accurate benzene analyses to be obtained. No benzene was formed in the absence of the base, whereas the addition of up to 6.5 equivalents of 2,6-di(*tert*-butyl)pyridine gave a 26 % yield of benzene. The stronger base, 2,6-lutidine, gave a still higher yield, 43 %, under otherwise identical conditions, and the formation of the DA dimer was almost completely suppressed (5 % yield). Under homogeneous conditions the results were closely similar, a 30 % yield of benzene using 2,6-di(*tert*-butyl)pyridine as the base. It should be kept in mind that the accuracy of this number is limited owing to the background level of benzene in the starting material.

Apart from the fact that there are literally hundreds of precedents for proton abstraction from radical cations,<sup>2-5</sup> a few cases specifically involving TBPA<sup>+</sup> as the oxidant and a 1,3-diene as the substrate are known. Thus  $\beta$ -ionone could be alkoxyated in the  $\alpha$ -position in dichloromethane/alcohol,<sup>22</sup> and 1,4-dimethyl-1,3-cyclohexadiene was oxidized to *p*-xylene in the presence of 2,6-di(*tert*-butyl)pyridine.<sup>23</sup> More generally, electrochemically induced DA reactions of 1-substituted 1,3-cyclohexadienes in the presence of 2,6-lutidine were accompanied by 10–55 % yields of the corresponding benzene derivatives.<sup>24</sup>

In the base-catalysed reactions, we detected no other volatile oxidation products which could account for the missing 60–70 % oxidation equivalents. We therefore suspected that oxidative oligomerization of CHD via its radical cation and/or 1,3-cyclohexadienyl cation was the missing oxidation process.<sup>25</sup> It has been shown<sup>25b</sup> that CHD is oligomerized to give a 70 % yield of a product with an average molecular weight of a decamer by TBPA<sup>+</sup> in dichloromethane at room temperature. We have repeated this experiment with 2 equiv. of 2,6-di(*tert*-butyl)pyridine present and obtained a small yield (ca. 20 %) of an oligomeric product, which according to MS analysis was the hexamer.

Thus benzene is a normal reaction product in the presence of a hindered pyridine base. The fact that it is not detectable in the absence of the base may to some extent be a reflection of the difficulty in analysing for very small amounts of benzene (level of safe detection  $\geq$  10 % yield), and predominantly due to diversion to another, unexpected pathway, formation of oxidative addition products from CHD<sup>+</sup>. This is a well-known reaction mode of radical cations,<sup>2-5</sup> much utilized in synthetic organic electrochemistry,<sup>3</sup> but not expected for the reaction at hand.

These products were 1,2- and 1,4-dichloro adducts of CHD, 3,4-dichlorocyclohexene and 3,6-dichlorocyclohexene, easily detectable by GLC and identified by GLC/MS based comparison with an authentic reaction mixture from the addition of chlorine to CHD by iodobenzene dichloride. As an example, a solution, 0.8 mM in TBPA<sup>+</sup> and 8.0

Table 2. Product composition vs. time in the reaction between 0.8 mM TBPA<sup>+</sup> SbCl<sub>6</sub><sup>-</sup> and 8.0 mM CHD in dichloromethane at 20 °C without or with added TBPA.

Time after mixing/min	Remaining CHD (%)	Product yield (%)		
		DA dimer ( <i>endo/exo</i> )	Oxidative chloro adducts	Trimers
No external TBPA added				
0.13	46.2	51.5(6.1)	2.0	0.3
0.5	24.2	71.5(6.8)	3.4	0.9
1	18.3	76.1(7.2)	4.0	1.1
2	13.3	82.2(7.1)	4.2	1.3
3	12.7	82.4(7.3)	4.5	1.2
5	7.2	84.6(7.5)	4.9	1.4
15	3.3	91.5(7.4)	5.6	1.6
30	2.0	89.7(7.7)	6.0	1.4
60	3.0	87.4(7.7)	5.8	1.4
External TBPA (0.8 mM) added				
0.15	73.3	25.9(5.4)	0.4	—
0.5	47.6	51.2(6.2)	2.2	0.3
1	37.8	59.0(6.5)	2.6	0.7
3	19.5	80.2(6.8)	3.8	0.9
5	16.6	83.5(6.6)	4.0	0.9
15	6.1	93.7(7.1)	5.2	1.3
30	3.8	94.0(7.1)	5.3	1.2
60	3.0	92.4(7.0)	5.5	1.1
120	0.2	94.0(7.2)	5.4	1.1

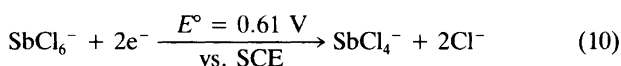
mM in CHD, after 15 min at 20 °C analysed for residual CHD (3 %), DA dimers (92 %, *endo/exo* = 7.4), oxidative chloro adducts (5.6 %) and also trimers (1.6 %), all yields of products being based upon unrecovered CHD. The yield of oxidative chloro adducts was essentially quantitative, based upon the amount of radical cation salt used. Almost identical results were obtained in the presence of added 0.8 mM TBPA. Table 2 shows the product development with time for these two reactions. As expected, addition of 2,6-di(*tert*-butyl)pyridine in a ratio of 1.1 or 2.0 with respect to TBPA<sup>+</sup> eliminated all oxidative chloro adducts and trimers. Another, less obvious way of eliminating the oxidative addition products and the trimers was found by adding an inert electrolyte, tetrabutylammonium hexafluorophosphate, in relatively high concentration (0.1 M). Blank experiments established that hexachloroantimonate (V) ion in itself (as its tetrabutylammonium salt) did not react with CHD under the reaction conditions used.

In principle, it is easy to explain the formation of chloro adducts by attack of chloride ion upon CHD<sup>+</sup>, followed by a second ET step and capture of a second chloride ion by the chlorocyclohexenyl cation. However, the source of chloride ion is not readily identified. Hexachloroantimonate(V) is a relatively stable ion, with a dissociation constant for the equilibrium  $\text{SbCl}_6^- \rightleftharpoons \text{SbCl}_5 + \text{Cl}^-$  in nitromethane of ca.  $10^{-15}$  M, which under our conditions translates into a  $[\text{Cl}^-]$  of ca.  $10^{-9}$  M at equilibrium.<sup>26</sup> Both thermodynamic and kinetic arguments militate against this

equilibrium being the source of free chloride ion. Moreover, the salt does not contain chloride ion as a significant impurity, as testified by the fact that the TBPA<sup>+</sup> SbCl<sub>6</sub><sup>-</sup> salt is itself completely stable in dichloromethane solution on the time scale of our experiments. TBPA<sup>+</sup> is known to react relatively fast with chloride ion (rate constant ca. 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> in acetonitrile<sup>8</sup>) and any chloride ion impurity in the solid salt would be mopped up by the radical cation upon dissolution.

Hexachloroantimonate(V) is the next obvious candidate as a chloride ion source for reaction with CHD<sup>+</sup> in a chloride transfer reaction. Such a reaction type is not entirely without precedents: chlorozincates have been implicated as chloride donors in the anodic chlorination of aromatics in dichloromethane,<sup>27</sup> and tetrafluoroborate ion has been shown to transfer fluoride ion in anodically induced fluorinations presumably occurring via radical cation intermediates.<sup>28</sup>

A third possibility resides in the fact that hexachloroantimonate(V) is a moderately strong, two-electron ET oxidant [eqn. (10)], capable of 'immediately' oxidizing, for example, triphenylamine ( $E^\circ \approx 1$  V) to its radical cation in



dichloromethane.<sup>29</sup> At the Sb<sup>III</sup> level, chloro complexes of antimony are far more labile<sup>26</sup> (equilibrium constant of  $\text{SbCl}_4^- \rightleftharpoons \text{SbCl}_3 + \text{Cl}^-$  is ca. 10<sup>-4</sup> M) and surely capable of supplying chloride ion for reaction with CHD<sup>+</sup>. We checked this possibility by treating tetrabutylammonium hexachloroantimonate(V) with TBPA (the strongest reductant present in the system) in dichloromethane, but found no evidence for an ET reaction between these two species under the conditions employed in the catalytic reactions, nor at considerably higher concentrations. Attempts to determine the one-electron potential of the  $\text{SbCl}_6^-/\text{SbCl}_6^{2-}$  couple by cyclic voltammetry (CV) in dichloromethane or acetonitrile failed.<sup>30</sup> Scanning in the cathodic direction, there is a first cathodic peak at ca. -0.15 V vs. SCE which after reversal of the scan gave rise to an associated anodic peak at ca. 1.1 V. This originated from one or several unstable species ( $i_{pa}/i_{pc} = 0.1$  at 40 mV s<sup>-1</sup> and > 0.9 at 500 mV s<sup>-1</sup> in acetonitrile), presumably representing the reversal of eqn. (10) in which stepwise oxidation of the tetrachloroantimonate(III) ion regenerates hexachloroantimonate(V) ion, with transient chloroantimony species having enough time to undergo follow-up reactions at low sweep rates.

Concluding, we will assume that hexachloroantimonate(V) ion is the source of chloride ion in the oxidative chlorination process. In the following, we denote the disappearance of TBPA<sup>+</sup> due to the various types of reductive processes discussed above, the 'background reaction.'

*Estimates of ET rate constants in the TBPA<sup>+</sup> system.* The kinetic analysis below must, to some extent, rely on rate

Table 3. Redox parameters for relevant redox couples of this study, as determined in dichloromethane/0.1 M tetrabutylammonium hexafluorophosphate/2.5 vol % trifluoroacetic anhydride.

Couple	$E^\circ/\text{V vs. SCE}$	$\lambda(0)/\text{kcal mol}^{-1}$
TBPA <sup>+</sup> /TBPA	1.06	12
CHD <sup>+</sup> /CHD	1.66	60
(CHD) <sub>2</sub> <sup>+</sup> /(CHD) <sub>2</sub>	2.17	60

constant estimates by the Marcus treatment, and we therefore first consider these calculations. As detailed elsewhere,<sup>31,32</sup>  $\Delta G_{\text{ET}}^\ddagger$  is related to  $\Delta G_{\text{ET}}^\circ$  and  $\lambda$  (the reorganization energy) via eqn. (11).  $\log(k_{\text{ET}})$  can then be calculated from the Eyring equation. The reorganization energy

$$\Delta G_{\text{ET}}^\ddagger = \frac{\lambda}{4} (1 + \Delta G_{\text{ET}}^\circ/\lambda)^2 \quad (11)$$

for a heteroexchange ET step can be set approximately equal to the mean value of the  $\lambda(0)$  values of the self-exchange reactions involved. It should be noted that the Marcus treatment is strictly valid only for outer-sphere ET steps, defined as possessing < 1 kcal mol<sup>-1</sup> of electronic interaction energy (resonance energy) between the reacting species in the transition state.

The redox parameters to be used are given in Table 3. For both TBPA and CHD the potentials given are reversible ones, whereas that of the DA dimer is a peak potential and thus likely to be larger than the reversible one. Thus calculations were therefore also performed for two lower values of the latter potential, 2.12 and 2.07 V. The  $\lambda(0)$  values are less certain, in that the one for TBPA/TBPA<sup>+</sup> was taken to be the same as that of the corresponding 4-methyl analogue<sup>33</sup> (12 kcal mol<sup>-1</sup>) and those of CHD/CHD<sup>+</sup> and (CHD)<sub>2</sub>/((CHD)<sub>2</sub>)<sup>+</sup> were both taken to be 60 kcal mol<sup>-1</sup> by analogy with the values measured for polymethylaromatic radical cations.<sup>34</sup> This similarity is based upon the analogy between allylic and benzylic hydrogens; in the latter case large  $\lambda(0)$  values can be traced to extensive delocalization of charge into the benzylic C-H bonds. The same should be true for the allylic positions of CHD<sup>+</sup> and (CHD)<sub>2</sub><sup>+</sup>. In order to allow for liberal errors in a direction that would bias the rate constants in favour of Bauld's mechanism [eqns. (6)–(8)], calculations were also performed for lower values of the latter  $\lambda(0)$  values, 50 and 40 kcal mol<sup>-1</sup>. Due to the charge situation of the steps considered, no electrostatic correction terms need to be considered.

Table 4 shows the results of these calculations. In most cases the ratio between the rate constants between the ET steps of eqns. (9) and (8) are between 10<sup>5</sup> and 10<sup>7</sup> and it is only for the rather implausible assumption that  $\lambda(0)$  of both CHD<sup>+</sup>/CHD and (CHD)<sub>2</sub><sup>+</sup>/(CHD)<sub>2</sub> are as low as 40 kcal mol<sup>-1</sup>, that ratios below 10<sup>4</sup> are obtained. Under the prevalent experimental conditions the ratio [CHD]/[TBPA] is < 10<sup>2</sup> most of the time, except for a short initial period. Thus

Table 4. Estimated rate parameters for ET steps of interest in this study.

Step	$\lambda(0)/\text{kcal mol}^{-1}$	$\Delta G_{\text{ET}}^{\circ}/\text{kcal mol}^{-1}$	$\log(k_{\text{ET}}/M^{-1} \text{s}^{-1})$	$\log(\text{ratio})^a$
Eqn. (8): (CHD) <sub>2</sub> <sup>++</sup> + CHD	60	-11.8	3.9	
	60	-10.6	3.5	
	60	-9.5	3.2	
	50	-11.8	5.7	
	50	-10.6	5.3	
	50	-9.5	5.0	
	40	-11.8	7.4	
	40	-10.6	7.0	
	40	-9.5	6.7	
Eqn. (9), $k_3$ : (CHD) <sub>2</sub> <sup>++</sup> + TBPA	60	-25.6	10.4	6.5
	60	-24.4	10.3	6.8
	60	-23.2	10.2	7.0
	50	-25.6	10.8	5.1
	50	-24.4	10.7	5.4
	50	-23.2	10.6	5.6
	40	-25.6	11.0	3.6
	40	-24.4	11.0	4.0
	40	-23.2	10.9	4.2
Eqn. (6), $k_1$ TBPA <sup>++</sup> + CHD	36	13.8	-1.6	
	31	13.8	-0.9	
	26	13.8	-0.2	
Eqn. (6), $k_{-1}$ CHD <sup>++</sup> + TBPA	36	-13.8	8.5	
	31	-13.8	9.3	
	26	-13.8	9.9	

<sup>a</sup>Ratio between the estimated rate constants of eqns. (9) and (8), respectively.

for all cases shown in Table 4, the ET reaction of eqn. (9) outruns that of eqn. (8) by a factor of at least 100, probably much more, under actual experimental conditions.

Table 4 also gives calculated rate constants for the reaction between TBPA<sup>++</sup> + CHD and its reverse [ $k_1$  and  $k_{-1}$ , eqn. (6)]. A value of  $k_1$  of 40 M<sup>-1</sup> s<sup>-1</sup> is estimated below, 2–3.5 orders of magnitude larger than the calculated values in Table 4. This corresponds to an energy of 3–5 kcal mol<sup>-1</sup>. Such a difference between the calculated and experimental values is indicative of an inner-sphere ET transition state, in which an electronic interaction of 3–5 kcal mol<sup>-1</sup> (equal to the energy gap  $B$  in the Shaik–Pross CM model<sup>35,36</sup>) is present. The same idea, although differently phrased, is inherent in Kochi's CT theory of ET reactions.<sup>37,38</sup> In the latter treatment, a CT complex is initially formed as a precursor for the ET step.

*Kinetics of the background reaction in the presence of a base.* The reactions shown above to be responsible for the disappearance of TBPA<sup>++</sup>, a reversible ET step followed by a chloride ion attack upon CHD<sup>++</sup> (no base present) or proton transfer from it (hindered pyridine base added) is common in radical cation chemistry.<sup>2-5</sup> The second chemical step is often rate-determining owing to its bimolecularity and the very low concentration of the intermediate

radical cation, but cases are also known where the second oxidation step becomes rate-determining, resulting in overall second-order dependence on radical cation concentration.<sup>5</sup>

We have earlier<sup>39</sup> developed a method for analysis of a kinetic scheme involving an initial, reversible ET step, followed by rate-determining proton transfer by a three-parameter non-linear regression method which directly computes a parameter  $P(2)$  from absorbance/time data for the disappearance of TBPA<sup>++</sup>. This method can be applied to the case where a hindered pyridine base is present, since the required conditions that [CHD] be approximately constant during the run and  $\gg$  [TBPA<sup>++</sup>] and [base]  $\gg$

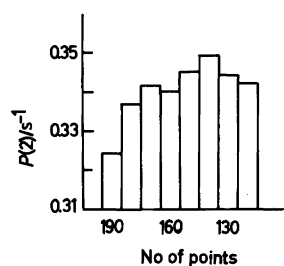


Fig. 4. Showing the variation of  $P(2)$  as data points are removed ten by ten from the beginning of the data set.

Table 5. Dependence of the first-order rate parameter  $P(2)$  upon  $[\text{CHD}]$  in the presence of 2,6-di(*tert*-butyl)pyridine, as determined by monitoring the disappearance of  $\text{TBPA}^{++}$  (as the hexachloroantimonate, fresh sample from previously unopened bottle) with time at 728 nm in dichloromethane at 20.0 °C.  $[\text{TBPA}^{++}]_0 = 0.4 \text{ mM}$ .

$[\text{CHD}]/\text{mM}$	$[\text{Base}]/[\text{TBPA}^{++}]$	$P(2)/\text{s}^{-1}$	$P(2)/[\text{CHD}]/\text{M}^{-1} \text{ s}^{-1}$
4.0	1.1	0.167	42
8.0	1.1	0.309	39
4.0	2.0	0.165	41
8.0	2.0	0.325	41
4.0	5.0	0.160	40
8.0	5.0	0.308	39
			40 (average value)

$[\text{CHD}^{++}]$  are fulfilled.  $P(2)$  is related to the rate constants  $k_1$ ,  $k_{-1}$  [eqn. (6)] and  $k_b$ , the rate constant representing attack by base upon  $\text{CHD}^{++}$ , via eqn. (12). Due to the approximations introduced in deriving this method, calculations must be performed on a set of data points where a certain value of the initial absorbance ( $Ab_{s_0}$ ) must not be exceeded, taken to be ca. 0.4 for the reactions at hand. Fig. 4 shows how  $P(2)$  converges towards a constant value as data points are removed ten by ten from the early part of the data set in one particular case. Under conditions where

$$P(2) = \frac{k_1 k_b [\text{CHD}][\text{base}]}{k_{-1}[\text{TBPA}]_{\infty} + k_b[\text{base}]} \quad (12)$$

a relatively strong base is present, the first term of the denominator becomes vanishingly small [eqn. (13)]. Table 5

$$P(2) = k_1[\text{CHD}] \quad (13)$$

shows kinetic data for this case; the rate of the background reaction is independent of added hindered [base] and approximately first order in  $[\text{CHD}]$  under these conditions, as predicted from eqn. (11). From eqn. (13) and the data of Table 5 a value of  $k_1 = 40 \text{ M}^{-1} \text{ s}^{-1}$  can be estimated.

In order to establish that the hindered pyridine bases do not undergo fast reactions of their own with  $\text{TBPA}^{++}$ , check experiments were performed in which  $\text{TBPA}^{++}$  (0.80 mM) was allowed to react with 2,6-di(*tert*-butyl)pyridine or 2,6-lutidine alone (16 mM in either). These were slow, pseudo-first-order reactions with rate constants equal to  $5 \times 10^{-4}$  and  $4.5 \times 10^{-4} \text{ min}^{-1}$ , respectively, i.e. much slower than the background reactions with no base added.<sup>9</sup>

*The kinetics of the DA dimerization reaction.* Under conditions where no external base is added, the dimerization of  $\text{CHD}$  proceeds rapidly, thus continuously changing  $[\text{CHD}]$  and removing one of the conditions for applying the method used above for analysing the kinetic data. The disappearance of  $[\text{TBPA}^{++}]$  also proceeds rapidly (Fig. 2) and it is of interest first to illustrate the interdependence of

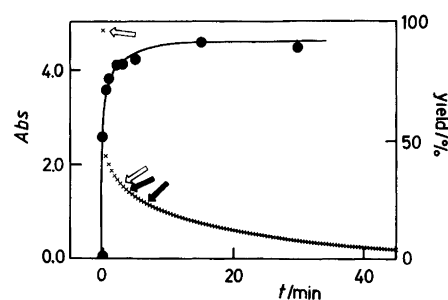


Fig. 5.  $\times$ ; Decay (monitored at 728 nm) of an initially 0.8 mM solution of  $\text{TBPA}^{++} \text{ SbCl}_6^-$  in dichloromethane at 20 °C upon addition of  $\text{CHD}$  in an initial concentration of 8.0 mM. The second reaction region is indicated but does not represent the solution actually reacting. The time dependence of DA dimer yield is given for the first data set of Table 2 (no  $\text{TBPA}$  added). Open arrows: beginning and end of first reaction period; filled arrows: beginning and end of second reaction period (see the text).

the two processes in a semiquantitative experiment. Fig. 5 shows a kinetic trace (recorded separately) of the decay of  $\text{TBPA}^{++}$  (0.80 mM with an initial absorbance of 4.83 at 728 nm in a 2 mm cell) with 8.0 mM  $[\text{CHD}]$  initially present. Half of this solution was quenched after 3 min at 20 °C and then gave a DA dimer yield of 74 % and 20 % recovery of  $\text{CHD}$ . The remaining solution was again made 8.0 mM in  $\text{CHD}$  (ca. 4 min after initiation of the experiment) and quenched after a further 3 min; this time the DA dimer yield was 71 %, with 24 % recovered  $\text{CHD}$ . Thus it seems as if the prevailing  $[\text{TBPA}^{++}]$  can vary by a factor of 3–4, as indeed it does in the two reaction regions of Fig. 5, without significantly influencing the rate of DA dimerization.

A remarkable feature of Fig. 5 (cf. also Fig. 2) is the very fast decay of  $\text{TBPA}^{++}$  during the first 30 seconds of the reaction, in that more than half the initial concentration has disappeared and been replaced by an equal concentration of  $\text{TBPA}$ . This is accompanied by an equally fast build-up of DA dimers (Fig. 5), a > 50 % yield being formed within the first 8 s of the reaction. Thus the DA dimerization process takes place under conditions of rapidly changing  $[\text{TBPA}^{++}]$  and  $[\text{TBPA}]$ , and it remains to analyse how one should treat the kinetics of DA dimerization under such circumstances.

One fact was obvious from an inspection of redox potentials of the species involved. The triarylamine,  $\text{TBPA}$ , is the most reactive reductant present in the system ( $E^\circ$  for oxidation = 1.05 V vs. that of  $\text{CHD}$ , 1.65 V), and it is formed in significant concentration very soon after the start of the reaction (Figs. 2 and 5). The Marcus treatment was used above (Table 4) to show that the reduction of  $(\text{CHD})_2^{++}$  by  $\text{TBPA}$  is more efficient than that by  $\text{CHD}$  by 5–7 powers of ten, and that eqn. (9) competes favourably with eqn. (6). We therefore postulate that the sequence of eqns. (6), (7) and (9), or rather, its equivalent in ion-pair formulation (see below), is the best representation of the

mechanism, i.e., a normal catalytic mechanism similar to, for example, proton catalysis, with the hole playing the role of the proton.

Application of the steady state approximation to  $[\text{CHD}^{\bullet+}]$  and  $[(\text{CHD})_2^{\bullet+}]$  to the kinetic scheme of eqns. (6), (7) and (9) eventually leads to eqn. (14) as the expression of the rate of disappearance of CHD. Under the conditions employed in the kinetic runs, the second term

$$-\frac{d[\text{CHD}]}{dt} = \frac{2k_1k_2[\text{CHD}]^2[\text{TBPA}^{\bullet+}]}{k_{-1}[\text{TBPA}] + k_2[\text{CHD}]} \quad (14)$$

of the denominator can be neglected and thus the simplified expression (15) is obtained. Rearrangement of eqn.

$$-\frac{d[\text{CHD}]}{dt} = \frac{2k_1k_2[\text{CHD}]^2[\text{TBPA}^{\bullet+}]}{k_{-1}[\text{TBPA}]} \quad (15)$$

(15), substitution of  $[\text{TBPA}]$  by  $([\text{TBPA}^{\bullet+}]_0 - [\text{TBPA}^{\bullet+}])$  and integration gives eqn. (16). The integral on the right-hand side represents 'reduced time',  $t'$ , and can readily be

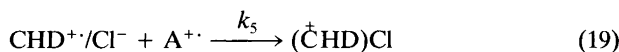
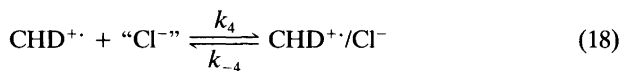
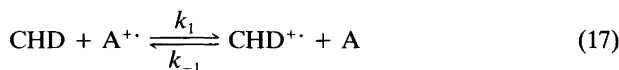
$$-\int_{[\text{CHD}]_0}^{[\text{CHD}]} \frac{d[\text{CHD}]}{[\text{CHD}]^2} = \frac{2k_1k_2}{k_{-1}} \int_0^{t'} \frac{[\text{TBPA}^{\bullet+}] dt}{([\text{TBPA}^{\bullet+}]_0 - [\text{TBPA}^{\bullet+}])} \quad (16)$$

evaluated by numerical integration from a suitable manipulated  $[\text{TBPA}^{\bullet+}]/t$  data set. The reduced time method is described in more detail in Ref. 40.

Application of this method to the  $[\text{CHD}]/\text{time}$  data of Table 2, in combination with the corresponding  $[\text{TBPA}^{\bullet+}]/\text{time}$  data set (200 points, recorded separately) indeed showed that a rate equation, second order in  $[\text{CHD}]$ , applied well when  $t'$  was used as the time variable. The rate constants  $[k(\text{CHD})_{\text{obs}}]$  obtained were 8.5(8) and 8.7(3)  $\text{M}^{-1} \text{s}^{-1}$ , the latter for the run in which 0.8 mM  $[\text{TBPA}]$  was present initially. Other rate expressions were tried, but did not fit.

Thus, in a hypothetical experiment in which the  $[\text{TBPA}^{\bullet+}]/[\text{TBPA}]$  ratio could be kept constant during the run, we would be able to record simple second order disappearance of CHD, with the rate constant  $[k(\text{CHD})_{\text{obs}}] \times [\text{TBPA}^{\bullet+}]_0/[\text{TBPA}]_\infty$ , the concentration quotient being required to accommodate differences in absolute levels of these concentrations.

*Kinetics of the background reaction without base added.* We can now return to the background reaction and use the second-order expression for the disappearance of  $[\text{CHD}]$  to derive the reduced time,  $t''$ , for these reactions and test various rate expressions for the disappearance of  $[\text{TBPA}^{\bullet+}]$ . The simplest kinetic scheme which could acceptably be fitted to such a data treatment is shown in eqns. (17)–(19), where TBPA has been replaced by A for brevity and 'Cl<sup>-</sup>' symbolizes the chloride ion source. This scheme corresponds to the well-established complexation mecha-



nism for reaction of radical cations with nucleophiles.<sup>4</sup> Application of the steady state treatment to  $[\text{CHD}^{\bullet+}]$  and  $[\text{CHD}^{\bullet+}/\text{Cl}^-]$  results in eqn. (20). At high  $[\text{A}]/[\text{A}^{\bullet+}]$  ratios the first term in the denominator will become dominant with the following reasonable assumptions:  $k_{-1}$  (Table 4),  $k_4$  (formation of the complex) and  $k_5$  (exergonic ET step) diffusion controlled =  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{-4}$  (dissociation of a complex of intermediate strength) =  $10^7 \text{ s}^{-1}$ ,  $[\text{A}^{\bullet+}]_0 \approx [\text{Cl}^-] \approx 10^{-3} \text{ M}$ , and  $[\text{A}^{\bullet+}] < 10^{-5} \text{ M}$ , so that eqn. (21) applies under these conditions. Introduction of  $[\text{A}] =$

$$-\frac{d[\text{A}^{\bullet+}]}{dt} = \frac{k_1k_4k_5[\text{Cl}^-][\text{CHD}][\text{A}^{\bullet+}]^2}{k_{-1}k_{-4}[\text{A}] + k_5[\text{A}^{\bullet+}](k_{-1}[\text{A}] + k_4[\text{Cl}^-])} \quad (20)$$

$$-\frac{d[\text{A}^{\bullet+}]}{dt} = \frac{k_1k_4k_5[\text{Cl}^-][\text{CHD}][\text{A}^{\bullet+}]^2}{k_{-1}k_{-4}[\text{A}]} \quad (21)$$

$([\text{A}^{\bullet+}]_0 - [\text{A}^{\bullet+}])$  and separation of the variables yields eqn. (22) which can be integrated to eqn. (23), keeping in mind that  $[\text{CHD}] = 1/([\text{CHD}]_0^{-1} + k(\text{CHD})_{\text{obs}}t)$  can now be integrated with respect to time. The advantage with eqn. (23) is that a set of the values of the expression to the left is

$$-\frac{d[\text{A}^{\bullet+}]}{[\text{A}^{\bullet+}]^2} ([\text{A}]_0 + [\text{A}^{\bullet+}]_0 - [\text{A}^{\bullet+}]) = \frac{k_1k_4k_5[\text{Cl}^-][\text{CHD}]}{k_{-1}k_{-4}} dt \quad (22)$$

$$([\text{A}]_0 + [\text{A}^{\bullet+}]_0) \left( \frac{1}{[\text{A}^{\bullet+}]} - \frac{1}{[\text{A}^{\bullet+}]_0} \right) + \log([\text{A}^{\bullet+}]/[\text{A}^{\bullet+}]_0) = \frac{k_1k_4k_5[\text{Cl}^-][\text{A}]_\infty}{k_{-1}k_{-4}k(\text{CHD})_{\text{obs}}[\text{A}^{\bullet+}]_0} \log \left( \frac{[\text{CHD}]_0^{-1} + k(\text{CHD})_{\text{obs}}t}{[\text{CHD}]_0^{-1}} \right) \quad (23)$$

easily obtained by transformation of the absorbance/time data and then can be plotted vs. reduced time [ $t'' =$  the logarithmic expression on the right-hand side of eqn. (23)]. This is expected to give a straight line at high  $[\text{A}]/[\text{A}^{\bullet+}]$  with the slope ( $S$ ) shown in eqn. (23). This is a dimensionless number. Observing that we have already derived that  $k(\text{CHD})_{\text{obs}} = 2k_1k_2/k_{-1}$  and that our previous deduction is that  $\text{SbCl}_6^-$  is the chloride ion source, the expression for  $S$  is simplified to eqn. (24). Fig. 6 shows a plot of a data set



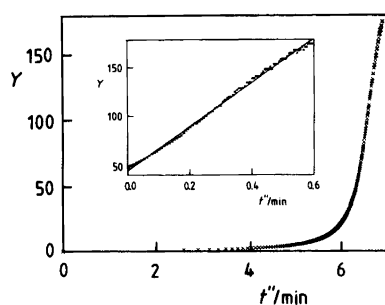


Fig. 6. Plot of  $Y = ([A]_0 + [A^{+\cdot}]_0)(1/[A^{+\cdot}] - 1/[A^{+\cdot}]_0) + \log ([A^{+\cdot}]/[A^{+\cdot}]_0)$  vs. reduced time ( $t''$ ), the insert demonstrating the linear behaviour of the last 90 data pairs ( $t''$  actually begins at ca. 6.2 min but was normalized to 0).

transferred according to eqn. (23) which indeed displays linear behaviour at high  $[A]/[A^{+\cdot}]$ . A number of kinetic

$$S = \frac{k_4 k_5 [A]_\infty}{2k_2 k_{-4}} \quad (24)$$

runs under different conditions gave the  $S$  values listed in Table 6. A plot of  $S$  vs.  $[TBPA]_\infty$  is shown in Fig. 7, displaying the expected linear dependence [slope  $1.5(1) \times 10^5 \text{ M}^{-1}$ ] and with an intercept ( $14 \pm 14$ ) on the  $y$ -axis almost equal to the expected zero. From this slope and the rate constants estimated above one can calculate a value of  $k_2 \approx 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , in satisfactory agreement with the value experimentally determined by Calhoun and Schuster,<sup>41</sup>  $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (this value may however be lower; see below).

The same approach has been applied to various other kinetic schemes but none of these resulted in any sensible

Table 6. Slopes ( $S$ ) of the linear relationships between  $([A]_0 + [A^{+\cdot}]_0)(1/[A^{+\cdot}] - 1/[A^{+\cdot}]_0) + \log ([A^{+\cdot}]/[A^{+\cdot}]_0)$  and reduced time ( $t''$ ) at high ratios of  $[TBPA]/[TBPA^{+\cdot}]$  under different conditions. The reactions were run in dichloromethane at 20.0°C and  $[TBPA^{+\cdot}]$  monitored at 728 nm.

$[CHD]_0/\text{mM}$	$[TBPA^{+\cdot}]_0/\text{mM}$	$[TBPA]_0/\text{mM}$	$S$
4.0	0.40	0	70
4.0	0.40	0	53
4.0	0.40	0.20	133
6.0	0.40	0	88
6.0	0.60	0	92
6.0	0.60	0	104
6.0	0.60	0.30	114
6.0	0.60	0.30	157
6.0	0.60	0.60	204
6.0	0.60	0.90	209
6.0	0.60	1.20	341
6.0	0.60	1.50	348
8.0	0.40	0	86
8.0	0.80	0	141
8.0	0.80	0.80	223
10.0	0.40	0	52
10.0	0.40	0	88

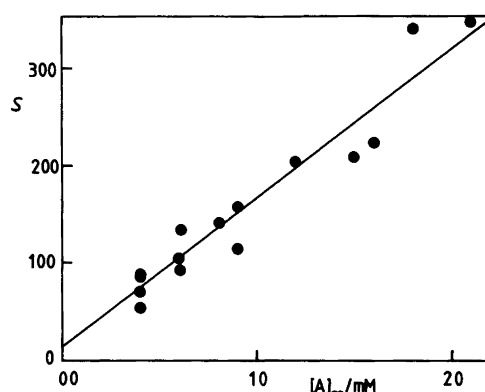


Fig. 7. Plot of  $S$  (see the text) vs.  $[A]_\infty/\text{mM}$ . The slope of the regression line is  $1.5(1) \times 10^5 \text{ M}^{-1}$  and the intercept on the  $y$  axis 14(14).

correlation at high  $[A]/[A^{+\cdot}]$ . Only when a second-order dependence of  $[A^{+\cdot}]$  was incorporated into the kinetic scheme did the resulting function behave in the expected way. Since this mechanism agrees well with those of other radical cation/nucleophile interactions,<sup>5</sup> we find it reasonable to conclude that the reactivity of  $TBPA^{+\cdot} \cdot SbCl_6^-$  in the presence of CHD is in line with normal radical cation behaviour, with some reservations concerning certain details of the catalytic step of the dimerization reaction. These will be discussed in a forthcoming paper.<sup>42</sup>

The experiment in which the addition of 0.1 M tetrabutylammonium hexafluorophosphate was shown to eliminate all oxidative addition products, indicates that ion-pair participation is crucial. Ion pairing is important in the chemistry of radical ion salts, especially in a low-dielectric medium such as dichloromethane, and we know that the  $TBPA^{+\cdot} \cdot SbCl_6^-$  salt exists as ion pairs in this solvent.<sup>43</sup> Thus it is likely that most of the 'free' ions depicted in the equations discussed above should be replaced by ion pairs. This does not change the overall mechanistic conclusions.

*Comparison between the catalysed and thermal DA dimerization of CHD.* The catalytic gain on going from the  $[CHD + CHD]$  to  $[CHD^{+\cdot} + CHD]$  dimerization step was estimated to be  $10^{23}$  from the activation enthalpy of a 'prototype' thermal DA reaction,  $34.3 \text{ kcal mol}^{-1}$ , and from an estimated activation enthalpy for the  $CHD/CHD^{+\cdot}$  step of  $1.6 \text{ kcal mol}^{-1}$ .<sup>6,16</sup> The rate constant of this step has been estimated to be  $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , assuming that the rates of the ET steps of eqn. (8) and between  $CHD^{+\cdot}$  and various 'selective quenchers' are diffusion controlled.<sup>41</sup> This assumption is strongly dependent upon the choice of  $\lambda(0)$  for the  $CHD^{+\cdot}/CHD$  homoexchange reaction (Table 4); with a value of  $50\text{--}60 \text{ kcal mol}^{-1}$  the rate constant of  $CHD^{+\cdot}/\text{quencher}$  will be of the order of  $10^6 \text{ M}^{-1} \text{ s}^{-1}$  and thus that of the  $CHD^{+\cdot}/CHD$  electrophilic interaction ca.  $10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

For the actual case of CHD, our liquid-phase value of the activation energy of the thermal reaction is  $22 \text{ kcal mol}^{-1}$ .

With the above value of the activation enthalpy of the radical cation/neutral step, its activation energy becomes  $1.6 + RT = 2.2 \text{ kcal mol}^{-1}$  and the actual catalytic gain at  $20^\circ\text{C}$  is ca.  $10^{15}$ , considerably smaller than the above estimate but still representing an impressive effect.

**Conclusions.** The  $\text{TBPA}^+/\text{CHD}$  system represents a formidable mechanistic problem, and further complications no doubt will surface in the future. The work described above has clarified the fate of the TBPA radical cation, insofar as we know that is spent by reduction to TBPA, in the process causing oxidative chlorination of CHD and/or oxidation of CHD to benzene/dehydro-oligomers. The oxidative chlorination process appears to proceed via the complexation mechanism. Since TBPA is already present in significant concentration in the reaction mixture in the initial phase, a conventional catalytic mechanism for the Diels–Alder dimerization of CHD is a likely alternative to the radical cation chain mechanism commonly postulated.

## Experimental

**General methods.** Most of these have been described in previous papers of this series.<sup>7–10</sup> Slow kinetics experiments were performed in a 2 mm cuvette, using an Ultraspec instrument (LKB, Sweden) interfaced to an HP-85 micro-computer. Two hundred data points were collected in each run and the kinetic parameters evaluated as described before.

**Materials.** Tetrabutylammonium hexachloroantimonate(V) was prepared as described for the tetraethylammonium salt<sup>29</sup> and recrystallized from ethyl acetate/cyclohexane (7:3). Anal.  $\text{C}_{16}\text{H}_{36}\text{Cl}_6\text{NSb}$ : C, H, N, Cl. 1,3-Cyclohexadiene was from Aldrich and used as received.  $\text{TBPA}^+\text{SbCl}_6^-$  was of commercial quality (Aldrich, 98%) and kinetic experiments were performed with salt from freshly opened bottles. As shown earlier for its reaction with charged nucleophiles,<sup>7,8</sup> the salt was prone to ageing, as shown by a significant variation of rate constants with storage time. This trend was also noticeable with CHD, the rate parameter  $P(2)$  decreasing from by a factor of ca. 3 upon storage of an opened bottle of the radical cation salt at  $0^\circ\text{C}$  for six weeks. Originally, this rate drift was ascribed to slow reduction of the salt to give TBPA, known to slow down the CHD reaction (see Table 2). However, all the salt specimens were checked by UV/VIS spectroscopy and showed identical spectra. It was also established that washing the crystals of an aged salt with dichloromethane, but not diethyl ether, restored its kinetic activity to the original value.

**Thermally induced dimerization of CHD.** Samples of CHD (neat, 200  $\mu\text{l}$  each) were kept in sealed Pyrex ampoules in an oven at  $120$  or  $200 \pm 1^\circ\text{C}$  and withdrawn at suitable intervals. The reaction was quenched by immersing the ampoule in an ice-bath and its contents were dissolved in

dichloromethane and analysed by GLC on a 10% Apiezon L column (2 m  $\times$  3 mm), using 1,4-diisopropylbenzene as an internal standard.

Reactions in dichloromethane were made on solutions 0.35 M in [CHD]. **WARNING!** These ampoules (25 ml) were cooled in a dry-ice bath before opening and still had a slight over-pressure.

**Radical cation induced dimerization of CHD.** The product studies of Table 1 were made under two sets of conditions: (1) following the directions given for preparative experiments ([CHD] = 190 mM,  $[\text{TBPA}^+] = 5 \text{ mol } \%$  of substrate, [hindered base] = 0–60 mM, dichloromethane,  $0^\circ\text{C}$ ; the radical cation salt is only partially soluble during the course of these experiments) and (2) under conditions of homogeneous solution ([CHD] = 9.2 mM,  $[\text{TBPA}^+] = 0.8 \text{ mM}$ , [hindered base] = 0–1.6 mM, dichloromethane,  $0^\circ\text{C}$ ). The reaction was started by adding the CHD via a syringe to a rapidly stirred mixture/solution of the remaining components and allowed to proceed for 15 min. After addition of an internal standard (toluene) the sample was passed through a short column of silica gel and then analysed by capillary GLC (25 m  $\times$  0.25 mm OV-1701 column). The polymerization experiment was carried out exactly as described in Ref. 25(b), except that two equivalents (relative to  $\text{TBPA}^+$ ) of 2,6-di-(*tert*-butyl)pyridine were added before the addition of the CHD. The yield of polymeric material after precipitation by methanol was ca. 80 mg (20%) and according to MS analysis was a hexamer of CHD.

The product studies reported in Table 2 were performed in the same way as before, except that the still kinetically active samples were quenched by addition of a 0.30 M solution of tetrabutylammonium iodide in dichloromethane (300  $\mu\text{l}$ ), followed by 300  $\mu\text{l}$  of aqueous thiosulfate solution (0.5 M) to remove iodine. After addition of an internal standard (toluene), the solution was passed through a short column of silical gel and analysed by capillary GLC as before.

Authentic samples of a mixture of dichloro adducts were prepared by iodobenzene dichloride promoted chlorination of CHD according to Ref. 44. A mixture of 3,4-dichloro- and 3,6-dichloro-cyclohexene was formed in the same proportions as reported. GLC/MS analysis showed that these compounds were identical with those obtained from the  $\text{CHD}/\text{TBPA}^+\text{SbCl}_6^-$  reactions.

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